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Electrochemical Oxidation of Methylene Blue using Lead Acid Battery Anode

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Abstract

In this paper, degradation of a basic dye (methylene blue), using electrochemical oxidation is studied. The chemical oxygen demand (COD) removal efficiency obtained under optimum conditions of present setup was 62%. The optimum operating conditions were 2V applied voltage, 0.01M NaCl concentration with 14 x 4 cm² immersed electrode area. Under optimum conditions the observed EC and CE are 82.35 KWH/Kg COD and 81.5% respectively.

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Keywords: Methylene Blue, degradation, COD, energy consumption, current efficiency

1. Introduction

Industries which use dyes and intermediates include food, cosmetic, pharmaceutical, tannery etc. [1, 2] but textile industry accounts for about 80% of dye stuff consumption. Coloured wastewater from the textile industry affects the ecosystem in many ways. Colour reduces penetration of light into the water bodies thus affecting the photosynthetic activity of aquatic plants resulting in reduction of dissolved oxygen [1]. Many of the synthetic dyes which are now in use are toxic and are proven as potential carcinogens [3].

One of the recent methods studied in this field of degradation of textile wastewater is electrochemical degradation of dyes developed in mid 90s. This, specially, electrochemical oxidation is one potential method for degradation of dyes. Electrochemical treatment of wastewater offers high removal efficiencies and has

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lower temperature requirements compared to non-electrochemical treatment. In addition, it could prevent the production of unwanted by-products and there is no need for addition of chemicals to the treated wastewater [4]. Electrochemical oxidation leads to complete oxidation of dyes and the final products are non-hazardous and hence secondary pollution possibilities are less. Mostly studied electrode material for electrochemical oxidation of dye is boron doped diamond electrode [5-8]. Other electrodes like Pb/PbO₂, Sn/SnO₂, Pt/Ti, Nb/Diamond [9] etc. are also studied.

Methylene blue (MB), C.I. 52015, also called Basic Blue 9 is one of the most important and widely used cationic dyes. It is a basic dye widely used as a stain in bacteriology, oxidation–reduction indicator, antidote to cyanide and an antiseptic in veterinary work. It is mainly used on bast (soft vegetable fibers such as jute, flax, and hemp) and to a lesser extent on paper, leather, and mordanted cotton. It dyes silk and wool but has very poor light fastness on these fibers [10, 11].

In this paper, electrochemical oxidation of MB using Pb/PbO₂ anode and mild steel cathode at different operating conditions are studied and discussed.

2. Materials and methods

MB was obtained from Merck specialties Pvt. Ltd., Worli, Mumbai and 1000 ppm stock solution was prepared by dissolving 1 g of dye in 1 L distilled water from which required dilutions were prepared. Sulphuric acid and sodium hydroxide were used to adjust the pH of solution and these chemicals were obtained from Merck Specialties Pvt. Ltd., Worli, Mumbai. Sodium chloride, used as supporting electrolyte, was obtained from S.D. Fine-Chem Ltd., Mumbai. All chemicals were of analytical reagent grade. Spectroquant TR 320 of Merck was used for COD analysis using closed reflux colorimetric method (Method 5220 D-APHA). pH meter was manufactured by Toshniwal Inst. Mfg. Pvt. Ltd., Ajmer.

Reactor was laboratory scale undivided electrolysis cell system of dimensions 20 x 20 x 10 cm³ made from acrylic sheets. Electrodes of sizes 14 cm x 10 cm (lead acid battery electrode) were used. The reactor was mounted on a magnetic stirrer (Remi, India) for stirring and the electrodes were supported by stands. A schematic diagram of the setup is shown in Fig. 2. AC to DC convertor with voltage and current measuring and controlling devices with a voltage range of 0 to 12 V and with a current range of 0 to 100 mA was purchased locally.

All the reactions were carried out using double distilled water. Dye solution of 20 ppm were chosen as working solution and known amount of supporting electrolyte (NaCl) was added. Two liter of solution was used for each run. The experiments were carried out at ambient temperature and samples were taken at a regular interval. Degradation was analyzed by calculating the COD removal using closed reflux colorimetric method.

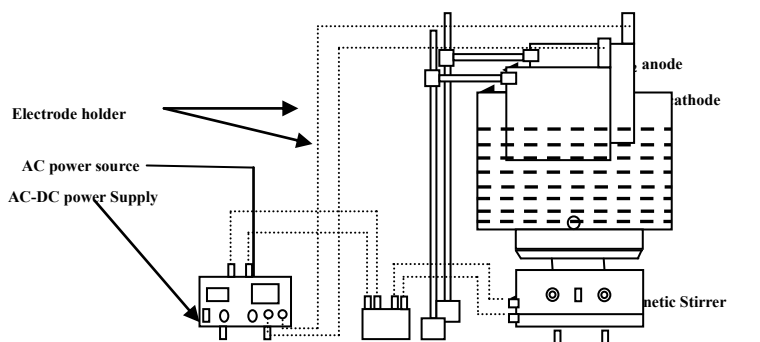


Fig. 1. Experimental Setup.

Current efficiency (Φ) is generally defined as the ratio of the charge used for the oxidation of each compound to the total charge passed during electrolysis [12].

$$CE = \left[\frac{COD_t - COD_{t+\Delta t}}{8I\Delta t} \right] Fv \quad (1)$$

Where COD_t , $COD_{t+\Delta t}$, are the COD at time t and $t + \Delta t$ [$\text{g O}_2 \text{ L}^{-1}$] respectively, I is the current (A), F is Faraday's constant [96487 C mol^{-1}], Δt is the time (S) and v is the volume of treated wastewater in L. The equivalent mass of oxygen is 8 [12].

The specific energy consumption, expressed in kWh kgCOD^{-1} , is the energy used to remove a unit mass of COD from wastewater and can be calculated using the following relationship [10].

$$EC = \frac{VI\Delta t}{\Delta COD \times v} \quad (2)$$

Where EC is the energy consumption in $\text{KWh per Kg COD reduced}$, V is the cell voltage (V), I is the applied current (A), Δt is the electrolysis time in hours and ΔCOD is the COD reduction in g L^{-1} during the time Δt and v is the volume of treated wastewater in L [10].

3. Results and Discussion

3.1. Effect of Supporting electrolyte (NaCl)

In the experiment, the effect of different concentration of NaCl for initial dye concentration of 20 ppm at a constant voltage of 1.5V on colour removal and COD reduction was studied. The effect of NaCl concentration on oxidation of MB is depicted in Fig. 2. For MB maximum COD reduction was obtained at 0.01M of NaCl and all further studies were conducted with 0.01M of NaCl. Higher efficiency is achieved with increased NaCl dose by increase in cell conductivity and hypochlorite ion production [13].

3.2. Effect of current density

The effect of current density was tested for an initial dye concentration of 20 ppm and NaCl dose 0.01M in the range 0.9 mA/cm^2 to 1.75 mA/cm^2 . The effect of current density on removal efficiency of MB is shown in Fig. 3. In the tested range as current density increased the removal efficiency shows an increasing trend. The increase in OH radical production with increase in current density caused in better degradation of organics at higher current density [14].

3.3. Effect of dye concentration

The influence of initial dye concentration on MB was investigated in the range of 10 ppm to 50 ppm since the degradation was slow. Tests were conducted at a chloride concentration of 0.01 M. An applied voltage of 1.5 V was used. COD reduction was independent of initial concentration in the range tested. The results of the experiments are plotted in Fig. 4. This emphasizes the fact that electrochemical oxidation can be used as a potential method for degradation of dyes irrespective of the concentration.

3.4. COD reduction and time

It was found that COD removal increases steadily with time. At 5 h under optimum conditions 62% COD

removal was observed for MB with a steady removal rate. No variation in removal efficiency was observed with change in pH which suggested that hydroxyl radical is the main oxidizing agent.

3.5. Current efficiency and Energy Consumption

Current efficiency (CE) and energy consumption (EC) was calculated for optimum conditions. Under optimum conditions the observed EC and CE are 82.35 KWH/Kg COD and 81.5% respectively. EC for MB is slightly high compared with other researches done [15]. This might be because of the highly recalcitrant nature of MB.

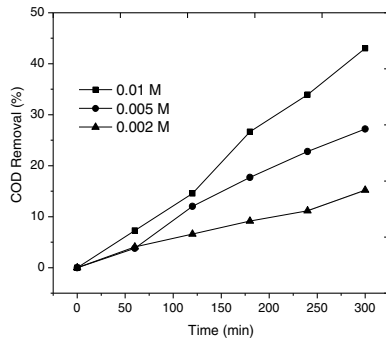


Fig. 2. Effect of NaCl on MB.

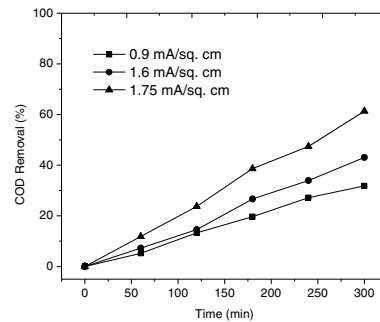


Fig. 3. Effects of current density on MB.

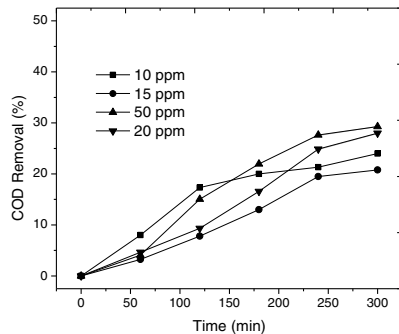


Fig. 4. Effect of Initial Dye concentration on MB.

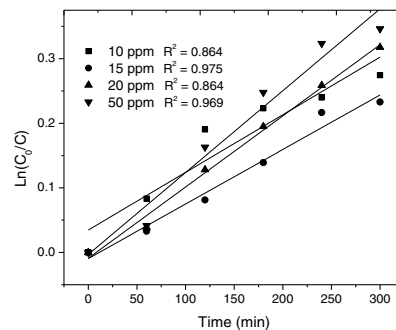


Fig. 5. Reaction Kinetics of MB.

3.6. Reaction Kinetics

The governing kinetic equation for colour removal can be written as considering both OH radical and chloride taking part in the reaction (equation 3). [3]

$$r_a = -\frac{d[C]}{dt} = k[C][Cl_2] \quad (3)$$

Since chloride is getting oxidized and reduced in the system continuously the concentration of Cl_2 can be assumed as a constant and the equation can be modified as equation 4

$$r_a = K_{app}[C] \quad (4)$$

The rate constant of the reaction is thus modified into the pseudo-first order rate constant K_{app} . The kinetics of the reaction was studied at different concentrations. It was found that the reactions were fitting well to pseudo-first order kinetics.

4. Conclusion

The feasibility of applying one of the recently developed and promising methods of dye removal, electrochemical oxidation, on MB was studied. Also a cost effective electrode material, i.e. anode of lead acid batteries was used as the electrode for the reaction. It was underlined that this method holds promise to be developed as a feasible method for treatment of real textile wastewater. The maximum COD removal obtained was 62 %. The optimum conditions for MB were 2V applied voltage, 0.01M NaCl concentration with 14 x 4 cm² electrode area.

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